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14. ABSTRACT

A novel breathing sphere model was developed in order to make microscopic molecular dynamics simulations tractable for laser ablation. The results of the simulations have allowed us to distinguish between desorption and ablation, predict velocity distributions of ablated particles, predict the fluence dependence of the ablation yield, explain the forward peaked angular distributions and predict the acoustic pressure wave characteristics. Numerous favorable comparisons with experimental data have been made.

15. SUBJECT TERMS

Laser ablation, molecular dynamics, breathing sphere model, matrix assisted laser desorption ionization (MALDI)

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FINAL REPORT
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OBJECTIVE: To investigate microscopic mechanisms and dynamics of FEL initiated ablation with a focus on multicomponent materials and effects of selective targeting of the laser energy.

APPROACH: We are developing a multiscale computational technology that includes atomistic, mesoscopic/molecular and continuum levels of description of fundamental processes involved in FEL laser ablation of biological materials. To date we have implemented a novel mesoscopic breathing sphere molecular dynamics (MD) model for organic solids, a bead-and-spring model for embedded biological and polymer molecules in an organic solid, and an atomic level model of water and small peptides. Recently we have initiated studies of incorporating photochemical reactions into the breathing sphere model and blending the breathing sphere model for short-time plume dynamics with direct simulation Monte Carlo (DSMC) methods for long-time plume dynamics.

ACCOMPLISHMENTS: An extensive review of the key results of the breathing sphere model has been written for a special issue of the International Journal of Mass Spectrometry in honor of Franz Hillenkamp's 65^{th} birthday [18]. In this paper we focus on direct comparisons of the results from the simulations with experimental data and on establishing links between the measured or calculated parameters and the basic mechanisms of molecular ejection. The results on the fluence dependence of the ablation/desorption yields and composition of the ejected plume are compared with mass spectrometry and trapping plate experiments, implications of the prediction of a fluence threshold for ablation are discussed. The strongly forward-peaked velocity and angle distributions of matrix and analyte molecules, predicted in the simulations, are related to the experimental distributions. The shapes and amplitudes of the acoustic waves transmitted from the absorption region through the irradiated sample are compared to recent photoacoustic measurements and directly related to the ejection mechanisms.

An elaborate modeling effort was undertaken to develop and implement the strategy for incorporating the photochemical reactions into the breathing sphere MD model in order to unravel the cooperative effects of thermal and photochemical mechanisms [10, 13, 15]. The initial system investigated is UV irradiation of chlorobenzene because of available experimental data and relatively simple photochemistry. Photochemical reactions

induced by the laser irradiation are found to release additional energy into the irradiated sample and decrease the average cohesive energy, therefore decreasing the value of the ablation threshold.

A long term goal of this project is to blend the mesoscopic MD model with a larger scale model such as direct simulation Monte Carlo (DSMC) so that we can follow the plume dynamics on extended time and length scales. In order to adopt the results of the breathing sphere MD model at 1 ns time for the DSMC, we must fully characterize the plume during the plume development. An extensive analysis of the ablated plume has been made [19] and the initial strategy for incorporating the information on the ablation plume parameters obtained from the MD simulations into the DSMC simulations has been made [17].

SIGNIFICANCE: Our simulations give a unique opportunity to study the laser ablation phenomena at molecular level and compose an important part of the effort to better understand the mechanisms of laser damage/desorption/ablation at a microscopic level. The insight provided into these physical processes can help in developing medical applications of FEL.

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